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(54) Inhibition of corrosion

(57) A method for inhibiting corrosion of steel materials used for a carbon dioxide gas removing apparatus, characterized in that, in a process of absorbing and removing carbon dioxide gas in a synthesis gas using as an absorber an aqueous carbonate solution, 1-hydroxyethylidene-1, 1-diphosphonic acid is added to the aqueous carbonate solution. According to this method, corrosion of steel materials can be inhibited without using conventional Na_2CrO_4, V_2O_5, etc. that are subject to control of pollutants.

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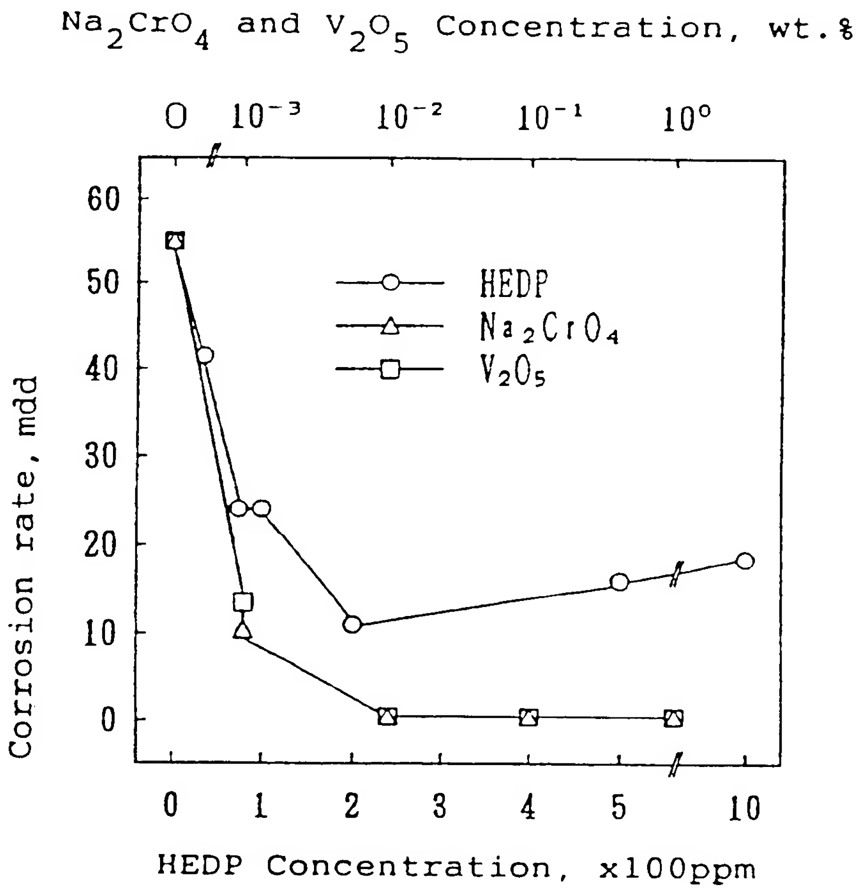
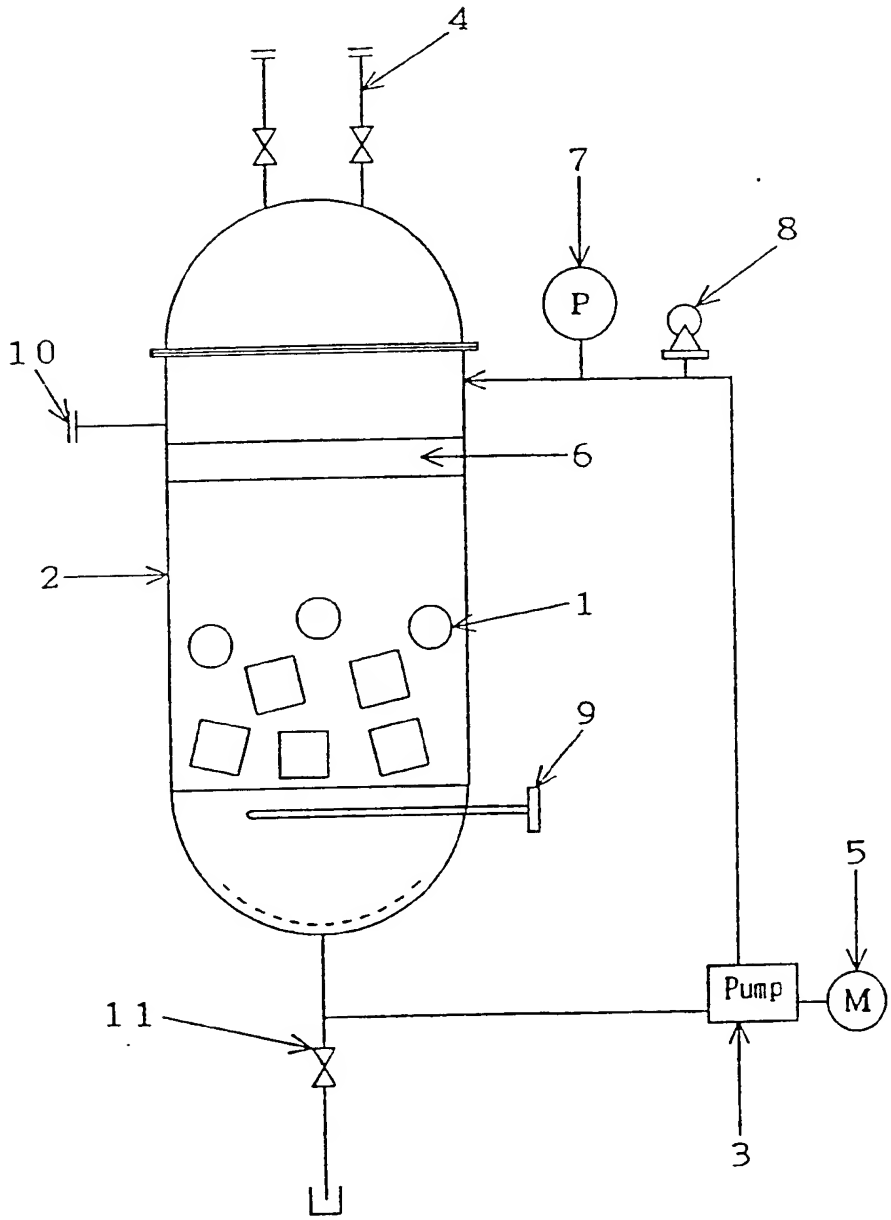
FIG. 1



Na_2CrO_4 and V_2O_5 Concentration, wt.%
0
10^{-3}
10^{-2}
10^{-1}
10^{0}
HEDP
Na_2CrO_4
V_2O_5
Corrosion rate, mdd
60
50
40
30
20
10
0
0
1
2
3
4
5
10
HEDP Concentration, x100ppm

FIG. 2



METHOD FOR INHIBITING CORROSION OF STEEL IN PROCESS OF ABSORBING CARBON DIOXIDE GAS

BACKGROUND OF THE INVENTION

The present invention relates to a method for inhibiting corrosion of steel materials used for apparatuses in processes of absorbing and removing carbon dioxide gas in various synthesis gases.

Prior Art

In the production of city gas, hydrogen gas, ammonia synthesis gas, and synthetic natural gas, for example by the steam reforming process, or the partial oxidation process using as raw material hydrocarbons such as petroleum, it is necessary to remove carbon dioxide gas that is an unrequired by-product.

These synthesis gases are mass-produced, their flow volume is high, and the carbon dioxide gas content is as high as 20 to 30 %. In order to remove economically carbon dioxide gas from such a synthesis gas whose flow volume is high and whose carbon dioxide gas content is high, leaving less residual content of carbon dioxide gas, there have been used at present a process that employs as an absorbing solution an aqueous potassium carbonate solution, and a process that employs as an absorbing solution an aqueous solution containing an amine such as monoethanolamine or diethanolamine.

Although the process using an aqueous solution of an amine is suitable for treating a gas whose carbon dioxide gas content

is small to lower the residual carbon dioxide gas content, the heat economy of the process is not good because the absorption liquid is cooled to be used. On the other hand, in the process that employs an aqueous solution of potassium carbonate, although the content of residual carbon dioxide gas is high, the heat economy is excellent because the absorbing solution is circulated without being cooled.

The process using an aqueous solution of potassium carbonate as an absorbing solution is known as the Ben-Field Process (Process Handbook edited by Sekiyu-gakkai "Acid Gas Removal, Ben-Field" (76/4) c, pp 1-4). In this process, absorption and release of carbon dioxide gas are carried out as shown by an equation below.

$$K_2CO_3 + CO_2 + H_2O \underset{\text{regeneration}}{\overset{\text{absorption}}{\rightleftharpoons}} 2KHCO_3 \qquad (I)$$

In an absorption tower, K_2CO_3 in the aqueous solution is converted into $KHCO_3$ so that the carbon dioxide gas is chemically absorbed, and in a regenerator, the $KHCO_3$ in the aqueous solution is converted to regenerate K_2CO_3 thereby releasing carbon dioxide gas.

The aqueous potassium carbonate solution that has absorbed carbon dioxide gas has corrosive properties, and had a problem that it corroded, although a little, steel materials used for the absorption tower, the regenerator, the pipelines connecting them, etc. including pipes, pumps, and control valves.

To prevent such a corrosion, an addition of corrosion inhibiting agents such as vanadium pentoxide (V_2O_5) and sodium chromate (Na_2CrO_4) to the potassium carbonate solution has been developed.

Although these vanadium pentoxide and sodium chromate are excellent in inhibition of corrosion, they are objects of control of pollutants, so that it is not preferable to use them for inhibiting corrosion. Further, although, in order to inhibit corrosion, stainless steels were used instead of carbon steels as the steel materials that are used for the absorption tower, the regenerator, pipelines connecting them, etc. the inhibition of corrosion was still not satisfactory, and it was desired to develop a pollution-free corrosion inhibiting agent in place of vanadium pentoxide and sodium chromate.

SUMMARY OF THE INVENTION

Therefore, the object of the present invention is to provide a method for inhibiting corrosion of steel materials by using a pollution-free corrosion inhibiting agent in a process of absorbing carbon dioxide gas.

The above object has been attained by a method for inhibiting corrosion of steel materials used for a carbon dioxide gas-removing apparatus, characterized in that, in processes of absorbing and removing carbon dioxide gas in a synthesis gas using as an absorber an aqueous carbonate solution, 1-hydroxy-ethylidene-1,1-diphosphonic acid is added to the aqueous

carbonate solution.

BRIEF EXPLANATION OF THE DRAWINGS

Fig. 1 is a graph showing corrosion exhibiting effects of corrosion inhibiting agents in a static system.

Fig. 2 is a schematic view of an apparatus for testing a corrosion weight loss in dynamic system.

DETAILED DESCRIPTION OF THE INVENTION

The process of absorbing and removing carbon dioxide gas used in the present invention is known as Ben-Field Process as mentioned above from an industrial point of view, and is practiced widely.

In the Ben-Field Process, as a carbonate, potassium carbonate is preferably used.

When potassium carbonate is used as an agent for absorbing carbon dioxide gas, the absorption and regeneration of carbon dioxide gas are carried out according to an equilibrium reaction represented by equation (I) mentioned above.

In this reaction system, by increasing the partial pressure of carbon dioxide gas, or lowering the temperature, the reaction proceeds toward the right, so that the carbon dioxide gas is absorbed, whereas by lowering the partial pressure of carbon dioxide gas, or elevating the temperature, the carbon dioxide gas is regenerated.

To absorb and regenerate carbon dioxide gas, for heat

economy it is advantageous to increase or lower the partial pressure of carbon dioxide gas than to elevate or lower the temperature of the absorbing solution.

Absorption and regeneration of carbon dioxide gas from a raw material gas can be carried out by known methods.

For example, absorption and regeneration of carbon dioxide gas can be carried out in an absorption tower and a regenerator that are filled with a packing such as Raschig rings, saddles, or poll rings.

Generally, a raw material gas is fed from the bottom part of an absorption tower and an absorbing liquid is flowed down from the top of the tower so that they may be brought in contact with each other by the gas-liquid countercurrent through the packing and the carbon dioxide gas may be absorbed and reacted to be removed from the raw material gas, and the thus purified raw material gas is taken from the top of the absorption tower. The absorbing solution leaving the bottom part of the absorption tower that has absorbed the carbon dioxide gas is fed into the top of a regenerator by using the pressure of the absorption tower. Part of the carbon dioxide gas absorbed in the absorbing solution is removed by vacuum flush at the top of the regenerator, and the absorbing solution flows down on the packing. The partial pressure of the carbon dioxide of the absorbing solution flowing down on the packing is lowered by the steam ascending from the bottom of the regenerator, and the potassium hydrogencarbonate in the absorbing solution is

decomposed into potassium carbonate and carbon dioxide gas. The thus produced carbon dioxide gas is removed from the top of the regenerator. The steam mentioned above may be generated by indirectly heating the absorbing solution by a reboiler located in the bottom of the regenerator, or may be live steam that will be supplied by blowing into the bottom of the regenerator directly. The steam supplies energy corresponding to the energy lost in the regeneration of the carbon dioxide gas.

As the absorption tower and the regenerator, a known absorption tower and regenerator can be used.

Although there is no particular limitation on the pressure and temperature at which the carbon dioxide gas is absorbed, generally a pressure of 10 to 30 kg/cm^2, and a temperature of 100 to 120°C are used industrially. Further, although there is no particular limitation on the concentration of the absorbing solution, generally the concentration is industrially selected to be in the range of 20 to 40 %.

The present carbon dioxide gas absorbing process that uses as an absorber an aqueous carbonate solution, and the present carbon dioxide gas separating process that uses as an absorber an aqueous carbonate solution may be used in combination with other carbon dioxide gas absorbing process or other carbon dioxide gas separating process, for example, a carbon dioxide gas absorbing process that uses an amine, or a carbon dioxide gas separating process that uses an amine.

In the present process, 1-hydroxyethylidene-1,1-diphosphonic

acid is added to an aqueous solution of a carbonate.

It is preferable that the amount of 1-hydroxyethylidene-1,1-diphosphonic acid to be added is 50 ppm or over, and more preferably 100 to 500 ppm.

The corrosion inhibiting effect of 1-hydroxyethylidene-1,1-diphosphonic acid is further increased if diethanolamine (DEA) is additionally used in a small amount.

The present invention will now be described with reference to the following Examples.

(1) Test of Corrosion Inhibiting Effect (Static System):

1-Hydroxyethylidene-1,1-diphosphonic acid (hereinafter referred to as HEDP), monoethanolamine (hereinafter referred to as MEA), diethanolamine (hereinafter referred to as DEA), triethanolamine (hereinafter referred to as TEA), propanolamine, Na_2CrO_4, V_2O_5, sodium molybdate (Na_2MoO_4), and sodium silicate (Na_2SiO_3) were added in amounts as indicated in Fig. 1 to an eggplant type flask containing 23 wt.% aqueous solutions of potassium carbonate saturated with carbon dioxide gas (temperature: 50 $\pm$ 1 °C). 20 x 50 x 1.6 mm Test pieces (steel, SS 41) whose surfaces had been abraded with emery paper (# 1500) and had been treated with methanol and acetone, were immersed in each of the eggplant type flasks containing the solution for 7 days at atmospheric pressure to perform a test of corrosion weight loss.

In the cases of MEA, DEA, TEA, propanolamine, Na_2MoO_4, and Na_2SiO_3, dark brown iron carbonate came about on the steel

surfaces, and any excellent corrosion inhibiting effect could not be obtained.

Results showing some corrosion inhibiting effect are shown in Fig. 1.

In the case of HEDP, although the effect was behind those of Na_2CrO_4 and V_2O_5 which are subject to control of pollutants, the corrosion inhibiting effect was such that when the concentration of HEDP was about 200 ppm, the inhibition efficiency (η) was 80 %.

(2) Test of Corrosion Inhibiting Effect (Dynamic System):

HEDP, DEA, Na_2CrO_4 and V_2O_5 were added in amounts as indicated in Table 1 to 40 wt.% aqueous solutions of potassium carbonate (temperature: 94 $\pm$ 4 °C). Each solution was circulated through a corrosion weight loss test apparatus on a bench scale (hereinafter referred to as BF apparatus) shown in Fig. 2 with the pressure kept at 10 kg/cm^2. Test pieces (steel, SUS 304) having an inner diameter of 23.6 mm, a thickness of 0.8 mm, and a height of 25.0 mm whose surfaces had been abraded with emery paper (# 1500) and had been treated with methanol and acetone, were immersed in each BF apparatus for 30 days so that the test of corrosion weight loss was effected.

Carbon dioxide gas was introduced into each BF apparatus to saturate the aqueous potassium solution with carbon dioxide gas.

In Fig. 2, test pieces 1 were placed in BF apparatus 2, and the aqueous potassium solution was circulated through the

BF apparatus by circulating pump 3. The aqueous potassium carbonate solution was saturated with carbon dioxide gas introduced from carbon dioxide gas inlet 4.

In Fig. 2, 5 indicates a motor for driving the circulating pump 3, 6 indicates a tray for allowing the aqueous potassium carbonate solution saturated with carbon dixoide gas to flow uniformly onto the test pieces 1, 7 indicates a pressure gauge, 8 indicates a safety valve, 9 indicates a thermometer, 10 indicates a peep hole, and 11 indicates a discharge valve.

Results obtained are shown in Table 1.

Table 1

Inhibiting agent and its amount	Weight loss (mg)	Corrosion rate (mdd) *1	Inhibition efficiency (%)
Blank	46.6	3.97	-
HEDP (100 ppm)	8.7	0.74	81.4
Na_2CrO_4 (0.1 wt.%)	0.6	0.06	98.7
V_2O_5 (0.1 wt.%)	1.8	0.15	96.2
DEA (3 wt.%)	12.5	1.06	73.3
HEDP (100 ppm) plus DEA (2 wt.%)	4.0	0.34	91.4

*1: $mg/dm^2 \cdot day$

In the case of HEDP, although the effect was behind those of Na_2CrO_4 and V_2O_5 that are subject to control of pollutants similarly to the test result of the above static system,

an excellent corrosion inhibiting effect was exhibited.

That corrosion inhibiting effect was further increased by allowing DEA to be present simultaneously.

Thus, according to the present invention, corrosion of steel material in a carbon dioxide absorbing process can be inhibited without using Na_2CrO_4, V_2O_5, etc. that have been conventionally used and are subject to control of pollutants.

CLAIMS

1. A method for inhibiting corrosion of steel materials used for a carbon dioxide gas removing apparatus, characterized in that, in a process of absorbing and removing carbon dioxide gas in a synthesis gas using as an absorber an aqueous carbonate solution, 1-hydroxyethylidene-1,1-diphosphonic acid is added to the aqueous carbonate solution.

2. The method for inhibiting corrosion as claimed in claim 1, wherein the carbonate is potassium carbonate.

3. The method for inhibiting corrosion as claimed in claim 1, wherein the amount of 1-hydroxyethylidene-1,1-diphosphonic acid to be added is 50 ppm or over.

4. The method for inhibiting corrosion as claimed in claim 3, wherein the amount of 1-hydroxyethylidene-1,1-diphosphonic acid to be added is 100 to 500 ppm.

5. The method for inhibiting corrosion as claimed in claim 1, wherein diethanolamine is added together with 1-hydroxyethylidene-1,1-diphosphonic acid to the aqueous carbonate solution.

6. Any novel feature or combination of features described herein.

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